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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for the Preparation of Level-Off DP Cellulose

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Process for the preparation of level-off DP cellulose

Abstract:

Level-off DP cellulose, which can be disaggregated in aqueous suspension with the application of mechanical force to give microcrystalline cellulose, is prepared by partial hydrolysis of cellulose in such a manner that the cellulose is subjected to partial hydrolysis in a pressurized reactor using water under a gas pressure of 0.1 to 60 bar of oxygen and/or carbon dioxide, measured at 20°C, at a temperature of 100 to 200°C until the levelling-off DP has been reached. The partial hydrolysis is preferably carried out under a gas pressure of 0.5 to 30 bar, measured at 20°C, and in a temperature range from 140 to 180°C.

Process for the preparation of level-off DP cellulose

Description:

Processes for the preparation of level-off DP cellulose have been disclosed (cf., for example, US-PS 2,978,446, US-PS 3,141,875 and US-PS 3,146,168). The term level-off DP cellulose, which was coined by O.A. Battista in his essay "Hydrolysis and Crystallization of Cellulose" in Industrial and Engineering Chemistry, Vol. 42 (1950), 502-507, and which has generally been accepted in expert circles, comprises celluloses which have been subjected to partial hydrolysis under mild conditions and whose degree of polymerization, which correlates closely with the crystallite size of the starting celluloses, is termed LODP (levelling-off degree of polymerization) and is in a range of approximately 30-400.

The known processes for the preparation of level-off DP cellulose basically include partial hydrolysis of cellulose under conditions at which it is only the amorphous areas of these partially crystalline polysaccharides which are attacked, but these are dissolved completely. The partial hydrolysis is carried out, in these processes, in an acidic medium using aqueous solutions of sulphuric acid, $FeCl_3$ and, preferably, of hydrochloric acid, the degree of polymerization during this treatment dropping down to the LODP, which, depending on the origin of the starting cellulose, can vary substantially. The resulting level-off DP cellulose is removed from the acid- or salt-containing mother liquor by means of filtration and subjected to laborious washing procedures to achieve an acid- or salt-free product involving a large amount of water and, if appropriate, using alkaline solutions, since the purity requirements stipulated for pharmaceutical purposes are very

stringent. A resuspension of the filter cake is followed by spray-drying, which gives the fine, flowable end product.

An important problem in the conventional processes is the large amount of polluted waste water. Characteristic of an already optimized process are the following amounts, which, however, are often exceeded by a factor of 2-3 under current practical conditions:

Total amount of water required	50 l/kg of level-off DP cellulose
NaCl obtained from the neutralized acid	80 g/kg of level-off DP cellulose
Hemicellulose obtained	60 g/kg of level-off DP cellulose
which corresponds to a COD of	64 g/kg of level-off DP cellulose

The object of the present invention is therefore to provide an environmentally friendly process for the preparation of level-off DP cellulose, by means of which the total amount of water required and hence the amount of waste water obtained per kg of level-off DP cellulose is drastically reduced and, in particular, the waste water obtained no longer contains inorganic salts. Another object of the present invention is to reduce the substantial amount of organic waste obtained and hence the COD value (Chemical Oxygen Demand) of the waste water resulting from the preparation process.

Surprisingly, it has been found that the object according to the invention can be achieved by a method in which, to prepare level-off DP cellulose, the cellulose is subjected to partial hydrolysis in a pressurized reactor using water under a gas pressure of 0.1 to 60 bar of oxygen and/or carbon dioxide, measured at 20°C, at a temperature of 100 to 200°C, until the levelling-off DP has been reached. Oxygen in the sense of the invention is also understood as meaning gas mixtures with inert gases which contain at least 20% by weight of oxygen, for

example air. If inert gases are present, the total pressure of such gas mixtures which is to be applied must be increased accordingly due to the partial pressures of the inert gases in order to reach the intended oxygen gas pressure.

A preferred embodiment of the process according to the invention comprises carrying out the partial hydrolysis under a gas pressure of 0.5 to 30 bar, measured at 20°C. To achieve high reaction rates and good colour values in the preparation of level-off DP cellulose, it is furthermore preferred that the partial hydrolysis is carried out in a temperature range from 140 to 180°C.

Suitable for the process according to the invention are, in principle, all purified celluloses which are prepared from the customary raw materials by conventional preparation processes. For example, the types of cellulose which can be used may have been produced from wood of coniferous trees, such as spruce, larch and pine, from woods of deciduous trees, such as beech, eucalyptus and birch, or from annual plants or other rapidly growing plants, such as cereal straw, bamboo and reed, by the sulphite pulping process, the sulphate pulping process or the nitric acid process for the production of cellulose. Alternatively, the purified celluloses may also have been obtained from cellulose-rich fibres, such as cotton, ramie, flax and hemp. Equally suitable are regenerated celluloses, such as rayon fibres and viscoses, and waste products of these. The LODP values which can be obtained by means of partial hydrolysis depend mainly on the choice of the abovementioned raw materials. In the case of partially hydrolysed cellulose types from woods of coniferous trees or deciduous leaves, from annual plants or from other rapidly growing plants, and in the case of partially hydrolysed purified celluloses from cellulose-rich fibres, the LODP values are approximately from 200-400, while regenerated celluloses give much lower LODP values, for example between 30 and 100.

Even the non-combination-type use of the required

gas pressures of oxygen or carbon dioxide allow the total amounts of water required in the preparation of level-off DP cellulose to be reduced by approximately 50%, i.e. from 50 l/kg, in the case of the conventional processes, to approximately 25 l/kg of level-off DP cellulose. Since the process according to the invention dispenses with the neutralization step and salts are no longer obtained as a by-product, the resulting waste-waters are accordingly free from salts. The sole use of oxygen or carbon dioxide also results in a noticeable reduction in COD values compared with the processes of the prior art, i.e. from 64 g/kg to approximately 30 g/kg to 50 g/kg of level-off DP cellulose. Furthermore, the partial hydrolysis of the cellulose under the sole gas pressure of oxygen from approximately 5 bar gives level-off DP celluloses which are not only distinguished by a noticeably lighter colour compared with the starting cellulose employed, but also give yields of more than 95% above the typical yield level of the conventional processes (90-95%).

A particularly preferred embodiment of the process according to the invention consists in subjecting the cellulose to partial hydrolysis under a gas pressure of oxygen and carbon dioxide. In this case the partial pressure of each type of gas is advantageously 30 to 70% of the total pressure. The combination of pure oxygen with carbon dioxide gives yields of level-off DP cellulose which exceed those from preparation processes of the prior art. While yields of 90-95% are typical for the latter, the combination according to the invention gives, generally, yields of 95-98%. In particular, however, the combination of oxygen and carbon dioxide generally results in COD values of only approximately 20 to 30 g/kg of level-off DP cellulose, so that the pollution of the waste-water resulting from the preparation process can also be reduced considerably with regard to the organic pollutants when compared with the conventional processes, independently of the fact that in this case too no more inorganic salts are added to the total amounts of water required in the process, which are

reduced by approximately 50% compared with the conventional processes, since neutralization is no longer necessary. Moreover, Elrepho colour values of the end product of above 80 can be achieved within the combination if an oxygen partial pressure from 2.5 bar is used, so that resulting level-off DP celluloses show a much lighter colour in comparison with the starting cellulose employed in each case.

In general, partial hydrolysis of the cellulose is carried out in conventional pressurized reactors which are equipped with a stirrer, for example a propeller stirrer, or another type of stirrer conventionally used in the cellulose-processing industry. The starting cellulose used is first chopped into chips, for example 5 x 5 x 1 mm in size, and excess water together with the chips is used to form an aqueous reaction liquor which, under the reaction conditions, is soon in the form of a fibre suspension (pulp). The liquor ratio can be varied within a wide range and can generally be from 1:3 to 1:40. As a rule, a liquor ratio from 1:8 to 1:20 is preferred for the process according to the invention. The reactor is usually filled with the aqueous reaction liquor to a degree of 50 to 90% of its nominal volume.

The pressurized reactor can be operated as a closed system so that the process according to the invention is, in this case, carried out batchwise. Since the gas used in the reaction is virtually unconsumed chemically, virtually all of it can be recirculated for subsequent batches. Alternatively, it is also possible to keep constant all flow operations with regard to quantity and quality and to operate the pressurized reactor fully continuously with the reaction conditions remaining constant over time. It is preferred within the scope of the invention for the reaction to be carried out in a continuously operated pressurized reactor.

Analogously to level-off DP celluloses which have been produced by conventional processes, for example using strong mineral acids, the level-off DP cellulose obtained by the process according to the invention meets

all requirements for pharmaceutical purposes and can therefore be employed, in particular, as an auxiliary for the production of tablets, as a stabilizer for suspensions or heat-stable O/W emulsions and in the food sector. If particle sizes of around 1 µm or below are desired for certain purposes, it is advantageous to disaggregate the level-off DP cellulose in aqueous suspension in a known manner with the application of mechanical force to give microcrystalline cellulose.

In the examples below, the oxygen or the carbon dioxide or the combination of the two gases were injected at room temperature after the pressurized reactor had been filled with liquor and then sealed, and, if the pressure dropped, for example by gas dissolving in the liquid, more gas was injected until the desired gas pressure values in the gas phase remained stationary. Accordingly, the gas pressures required always relate to the measuring temperature of 20°C. Finally, the reactor was brought to the reaction temperature by means of heat-transfer oil by means of its double jacket, always using approximately identical heating times, and the moment when the intended temperature was reached was considered as the beginning of the reaction time.

The following parameters were determined analytically on the level-off DP cellulose during the course of the process:

The yield was determined as the quotient of the two values weighed cellulose/weighed reaction product x 100%, in each case using materials which had been oven-dried under vacuum conditions.

The average degree of polymerization (= DP) was determined in agreement with DIN 54 270, parts 1 and 2.

The COD determination was carried out in agreement with DIN 38 409: "Deutsches Einheitsverfahren für Wasser/Abwasser und Flammpunktsverfahren [German standard process for water/waste water and flashpoint methods]".

The Elrepho colour value was determined using an apparatus manufactured by Zeiß, Oberkochen, "Elrepho" type, by a means of measuring the degree of remission of

the pulverulent sample with $BaSO_4$ as comparison substance, using filter R46. The measurement is carried out as described in DIN 53145.

The number of carboxyl groups (n_{COOH}), which can be regarded as a measurement for the oxidative damage to the cellulose, was determined by means of titrimetry using 0.1 N NaOH of a sample which has previously been treated with 1 N HCl and subsequently washed with fully demineralized water until neutral.

The relative crystallization characteristic (X_R) was determined similarly to the method of P.H. Hermans and A. Weidinger (J. Appl. Phys. 12 (1948) 491 or J. Polym. Sci. 4 (1949) 135). "Relative" in this context means that the numbers are comparable with regard to their relative deviation but do not represent absolute values. However, all of them differ merely by a constant factor from the corresponding absolute values (which would be accessible, for example, by a calibration series using substances of known, absolute crystallinity).

The invention is illustrated in greater detail with the aid of the examples which follow:

Example 1

The starting cellulose employed was a commercially available chemical pulp which had been prepared from northern spruce by the sulphite method and had an α-cellulose content of 92.2%, a DP of 1400, an Elrepho colour value of 79.4 and an X_R value of 0.66 as well as a COOH value of 20 mmol/kg. The pressurized reactor used was a 1 l laboratory-scale pressurized apparatus manufactured by BÜCHI and equipped with a stirrer. The reactor liquor was formed by the sheet-like cellulose cut into chips approximately 5 × 5 × 1 mm in size, in an excess of water, and the liquor ratio was 1:19. The reactor was filled with this reaction liquor to approximately 50% of its nominal volume. After the pressurized reactor had been sealed, 0.5 bar of carbon dioxide were injected at 20°C. The pressurized reactor was then brought to the reaction temperature of 160°C by means of a double jacket

using heat-transfer oil, and the point when this temperature was reached was considered as the beginning of the reaction time, which was 5 hours in the present case. After the reaction time had elapsed, the pressurized reactor was cooled to approximately 80°C in the course of approximately 60 minutes, the gas was discharged and the reactor then opened.

The reaction product was filtered off on a frit, and the filter cake was washed on the frit using approximately 5 l of de-ionized water per kg of dry level-off DP cellulose. In the wet state, the filter cake had the pasty, "loam-like" consistency which is characteristic of level-off DP cellulose. The COD values of the filtrate were measured, and the data obtained in mg/l were converted into g/kg of level-off DP cellulose obtained.

After drying overnight at 60°C and 20 mbar, the filter cake, which was then in the form of a hard, brittle block, was ground in a laboratory mill to give a fine, flowable product. The colour value, DP and relative crystallization characteristic (X_a) of this product were subsequently determined. The properties of the level-off DP cellulose obtained, the yield and the COD value were as follows:

Yield:	97.1%	COD (g/kg of end product):	28.1
DP:	295	Elrepho colour value:	78.8
X_a:	0.69		

Example 2

Example 1 was repeated, but the partial hydrolysis was carried out in this case under a carbon dioxide gas pressure of 5.0 bar. The properties of the level-off DP cellulose obtained, the yield and the COD value in g/kg of level-off DP cellulose were as follows:

Yield:	97.0%	COD (g/kg of end product):	48.5
DP:	302	Elrepho colour value:	78.2
X_a:	0.71		

Example 3

Example 1 was repeated, but the partial hydrolysis was carried out in this case under a carbon dioxide gas pressure of 10.0 bar. The properties of the level-off DP cellulose obtained, the yield, the COD value in g/kg of level-off DP cellulose and the carboxyl value were as follows:

Yield:	94.8%	COD (g/kg of end product):	36.7
DP:	318	Elrepho colour value:	78.5
X_n:	0.70	n_{COOH}:	12 mmol/kg

Example 4

Example 1 was repeated with several modifications, so that the reaction temperature was 160°C and the reaction time 2 hours. The partial hydrolysis, or the reduction of the average degree of polymerization, was furthermore carried out under an oxygen gas pressure of 2.5 bar. The properties of the level-off DP cellulose obtained, the yield and the COD value in g/kg of level-off DP cellulose were as follows:

Yield:	92.7%	COD (g/kg of end product):	31.9
DP:	303	Elrepho colour value:	79.2
X_n:	0.71		

Example 5

Example 4 was repeated, but the reduction of the average degree of polymerization was carried out under an oxygen gas pressure of 5.0 bar. The properties of the level-off DP cellulose obtained, the yield and the COD value in g/kg of level-off DP cellulose were as follows:

Yield:	95.9%	COD (g/kg of end product):	30.5
DP:	313	Elrepho colour value:	82.9
X_n:	0.71		

Example 6

Example 4 was repeated, but the partial

hydrolysis was carried out in this case under a oxygen gas pressure of 10.0 bar. The properties of the level-off DP cellulose obtained, the yield and the COD value in g/kg of level-off DP cellulose were as follows:

Yield:	97.0%	COD (g/kg of end product):	29.4
DP:	305	Elrepho colour value:	83.4
X_A:	0.71		

Example 7

In this example, the partial hydrolysis of cellulose Temalfa 93 was carried out in analogy to Example 4 using a combination of oxygen and carbon dioxide. The reaction temperature was therefore 160°C and the reaction time 2 hours. The partial pressure of both the oxygen and the carbon dioxide was 2.5 bar. The experiment was otherwise carried out as in Example 1. The properties of the level-off DP cellulose obtained, the yield, the COD value in g/kg of level-off DP cellulose and the COOH value were as follows:

Yield:	98.2%	COD (g/kg of end product):	28.5
DP:	318	Elrepho colour value:	80.8
X_A:	0.72	n_{COOH}:	13 mmol/kg

Example 8

Example 7 was repeated, but the partial pressures of the oxygen and of the carbon dioxide were 5.0 bar in each case. The properties of the level-off DP cellulose obtained, the yield, the COD value in g/kg of level-off DP cellulose and the COOH value were as follows:

Yield:	96.1%	COD (g/kg of end product):	20.9
DP:	312	Elrepho colour value:	81.6
X_A:	0.72	n_{COOH}:	14 mmol/kg

Example 9

Example 7 was repeated, but the partial pressures of the oxygen and of the carbon dioxide were 10.0 bar in

each case. The properties of the level-off DP cellulose obtained, the yield and the COD value in g/kg of level-off DP cellulose were as follows:

Yield:	95.3%	COD (g/kg of end product):	30.1
DP:	308	Elrepho colour value:	84.1
X_n:	0.71		

Example 10

In this example, the partial hydrolysis of the cellulose was carried out in a 3 l BÜCHI laboratory-scale stirred autoclave at a reaction temperature of 180°C and over a reaction time of 15 minutes using a combination of oxygen and carbon dioxide. The partial pressure of both the oxygen and the carbon dioxide was 2.5 bar measured at 20°C, and the total pressure at the reaction temperature of 180°C was 20.6 bar. The experiment was otherwise carried out as in Example 1. The properties of the level-off DP cellulose obtained, the yield, the COD value in g/kg of level-off DP cellulose and the COOH value were as follows:

Yield:	95.4%	COD (g/kg of end product):	31.4
DP:	315	Elrepho colour value:	83.1
X_n:	0.69	n_{COOH}:	12 mmol/kg

Example 11

Example 10 was repeated, but the partial hydrolysis was carried out in this case under an oxygen gas pressure of 5.0 bar measured at 20°C and with a liquor ratio of 1:10. The total pressure at the reaction temperature of 180°C was 17.9 bar during a reaction time of 15 minutes. The properties of the level-off DP cellulose obtained, the yield and the COD value in g/kg of level-off DP cellulose were as follows:

Yield:	95.8%	COD (g/kg of end product):	43.8
DP:	308	Elrepho colour value:	81.3
X_n:	0.70		

Example 12

In a technical laboratory experiment, the partial hydrolysis of the cellulose was carried out on a 100 l scale at a liquor ratio of 1:19 under an oxygen gas pressure of 5.0 bar, measured, as always, at 20°C. The reactor used in this case was 150 l pressurized titanium autoclave manufactured by Friedrichsfeld, equipped with an inclined-blade stirrer. Again, the autoclave was heated by means of a double jacket using heat-transfer oil. The reaction temperature was 180°C, the total pressure at this temperature 17.0 bar and the reaction time 0.5 hour.

After the reaction product obtained had been subjected to centrifuge washing using 5 l of water/kg of product, it was spray-dried and subjected to a specification test as described in US Pharmacopeia for microcrystalline cellulose for pharmaceutical purposes. The results obtained are shown in the table which follows in comparison with the established, commercially available product Avicel PH 101, which is manufactured by the US company FMC Corp., Philadelphia:

Table 1: Specification test for level-off DP celluloses
Specifications in accordance with US Pharmacopeia XXI, NF XVI, p. 1546

Specification		Commercially available comparison substance (Avicel PH 101)	Sample obtained by process according to the invention (Example 12)
Particle sizes			
< 1% 250 µm		0.0%	0.2%
< 30% 75 µm		9.9%	16.2%
Average diameter (µm)	•	45.1	47.6
Water			
< 6% by weight		4.5%	4.7%
pH			
5.5 - 7.0		6.1	5.5
Water-soluble components			
< 0.16% by weight		0.13%	0.07%
Ether-soluble components			
< 0.05% by weight		0.005%	0.003%
Starch			
Not detectable		•	•
Sedimentation			
Not observed over 3 hours		•	•
Ash			
< 0.1% by weight		0.05	0.03
Elrepho degree of whiteness	•	78.8	82.6
Chloride [ppm]	•	140	78
DP	•	283 ± 10	295 ± 10

• = meets specification
• = no specification in accordance with US Pharmacopeia, but important comparison parameter

Accordingly, the product obtained in Example 12 can be considered as superior to the comparison product

in some aspects. The remaining properties of the level-off DP cellulose obtained were as follows:

Yield:	93.3%	COD (g/kg of end product):	41.6
DP:	295	Elrepho colour value:	82.6
X_n:	0.73		

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. Process for the preparation of level-off DP cellulose by partial hydrolysis of cellulose under conditions at which it is only the amorphous areas of these partially crystalline polysaccharides which are attacked, but these are dissolved completely, which process is characterized in that the cellulose is subjected to partial hydrolysis in a pressurized reactor using water under a gas pressure of 0.1 to 60 bar of oxygen and/or carbon dioxide, measured at 20°C, at a temperature of 100 to 200°C, until the levelling-off DP has been reached.

2. Process according to Claim 1, characterized in that the partial hydrolysis is carried out under a gas pressure of 0.5 to 30 bar, measured at 20°C.

3. Process according to one or more of Claims 1 to 2, characterized in that the partial hydrolysis is carried out in a temperature range from 140 to 180°C.

4. Process according to one or more of Claims 1 to 3, characterized in that the cellulose is subjected to partial hydrolysis under a gas pressure of oxygen and carbon dioxide.

5. Process according to Claim 4, characterized in that the partial pressure of each type of gas is 30 to 70% of the total gas pressure.

6. Process according to one or more of Claims 1 to 5, characterized in that the cellulose is employed in an aqueous reaction liquor at a liquor ratio from 1:3 to 1:40.

7. Process according to Claim 6, characterized in that the liquor ratio is 1:8 to 1:20.

8. Process according to one or more of Claims 1 to 7, characterized in that the reactor is filled to a

degree of 50 to 90% of its nominal volume.

9. Process according to one or more of Claims 1 to 8, characterized in that the reaction is carried out in a continuously operated reactor.

10. Process according to one or more of Claims 1 to 9, characterized in that the level-off DP cellulose is disaggregated in aqueous suspension with the application of mechanical force to give microcrystalline cellulose.